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Preliminary study of the biorefinery concept to obtain furfural and binder-less panels from hemp (*Cannabis Sativa* L.) shives

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Abstract

The objective of the study was to investigate the preliminary technological parameters for obtaining furfural and binder-less panels depending on hydrothermal pre-treatment temperature, steam explosion treatment and pressing conditions. If the pre-treatment temperatures were 160–180 °C and the time 90 min, the yield of furfural was 64.8–67.2 % from that which was theoretically possible. The furfural obtaining dynamics significantly increases in the first 10 minutes, when the yield of furfural at 180 °C is almost twice as high as at 160 °C. The obtained maximal MOE value (3250 N mm^{-2}) and good enough surface of some panels demonstrate that all prepared hemp shives materials can be used for binder-less panel production. The obtained excellent correlation between MOE and MOR values (r = 0.9) demonstrates that the strength of the composites could be predictable.

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Keywords: hemp shives; hydrothermal pre-treatment; furfural; steam explosion; binder-less panels

1. Introduction

The utilisation of wood resources for energy production makes up the demand for the development of new technologies in the area of the chemical processing of agricultural residue (hemp shives, canola straw, etc.). The increasing demand for products derived by the chemical industry also increases the demand for furfural, which is exclusively produced from hemicelluloses-containing biomass [1]. There is no synthetic route available for furfural

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production in the chemical industry. The production of furfural belongs to environmentally friendly technologies, although it has chemical properties similar to those of petrochemicals. It is used for the production of a wide range of important non-petroleum derived chemicals such as furan, tetrahydrofuran and furfuryl alcohol [2]. It is also used as an extractive, a fungicide, in oil refineries, as well as in the plastics, food, pharmaceutical and agricultural industries [3]. For example, it can be introduced during fibril formation to enhance the thermal and mechanical stability of collagen [4]. At the moment, in the European Union, furfural is an imported products, although potential raw material resources are in a sufficient amount [5].

During hydrothermal pre-treatment, the dehydration of xylose to furfural in water typically proceeds at 150–220 °C, and the reaction rate is small under neutral conditions, increases during autocatalysis by acetic acid, which originates from the biomass, and is accelerated further by the addition of catalysts, especially strong acids such as sulphuric acid [2] or solid acid catalysts such as H-Beta zeolite [6]. The costs and inefficiency of separating these catalysts from the products make their recovery impractical, resulting in large volumes of acid waste, which must be neutralised and disposed of. Other drawbacks include corrosion and safety problems. $Al_2(SO_4)_3$ as a hydrolysis catalyst has been considered in some publications related to obtaining levulinic acid from biomass [7, 8], but there are no scientific publications about the use of $Al_2(SO_4)_3$ in furfural production from lignocellulosic biomass by hydrothermal pre-treatment. Furfural production from hemp (*Cannabis sativa* L.) shives has not been investigated until now as well, while the high content of hemicelluloses (see Table 1) shows that the hemp fibre production by-product has great potential. Also, this valuable raw material is concentrated in one place at the fibre production manufacturer's site. The hemp species are an approved and rapidly expanding crop in Latvia, with a yield from 150 ha in 2009 to 1200 ha in 2013. Hemp shives are the woody inner part of the hemp stalk separated from the fibres, making up to 75 % of the oven dry stalk. The chemical components of the hemp variety "Bialobrzeskie" shives used for experiments (Table 1) testify that the material also has the potential for the production of composites. Up until now, however, the main utilisation of hemp as a crop has been for its bast fibres [9]. To utilise the leftover lignocellulose after obtaining furfural, binder-less panels could be made without the use of any additional adhesives during the panels' production process. The panels made from the shives after the catalysed pre-treatment may have improved water resistance of the panel because hemicelluloses are the most water absorbing component [10] and, after pre-treatment, their content is significantly diminished. Furthermore, steam explosion treatment transforms the lignin structure in the plant matrix and promotes the binder-less composite moulding in the following hot-pressing process [11–13].

Table 1. Chemical and elemental analysis of "Bialobrzeskie" hemp shives

Chemical component	Percentage	Elemental analysis	Percentage
Cellulose	43.7 ± 0.4	Nitrogen	0.6 ± 0.03
Holocellulose	75.5 ± 0.8	Carbon	47.4 ± 0.08
Hemicelluloses	31.8 ± 0.7	Hydrogen	5.3 ± 0.05
Lignin	22.0 ± 0.6	Sulphur	0.2 ± 0.01
Minerals (ash)	1.6 ± 0.1	Oxygen (by difference)	46.8 ± 0.15
Pectin, wax	1.2 ± 0.1		

The objective of the study was to investigate the preliminary technological parameters of obtaining furfural and binder-less panels depending on the hydrothermal pre-treatment temperature, steam explosion treatment and pressing conditions. The pre-treatment process reference criteria for optimal parameters were chosen by the furfural yield and cellulose destruction degree in the leftover lignocellulose, which affects the obtained panel's mechanical properties. The panel's evaluation criteria were the panel quality and the maximal values of the tested properties – modulus of rupture (MOR) and modulus of elasticity (MOE).

2. Material and methods

2.1. Raw material

For the investigation of preliminary technological parameters of the processing of hemp shives, the hemp variety "Bialobrzeskie" (Poland, code 893) was chosen as a raw material. The chemical and elemental composition given in Table 1 was determined as described in [14]. The raw material was fractionated by a MUOTOTERA OY classifier using 5 screens according to SCAN-CM 40:01 [15]. For further processing, the fraction 3–12 mm, which comprises 77 % of the residues of hemp fibre production, was used to homogenise the raw material and to avoid the presence of undesirable compounds such as sand and long fibres.

2.2. Hydrothermal pre-treatment process

The process flow diagram is given in Fig.1. The hydrothermal pre-treatment process of hemp shives was carried out in a specially constructed 13.7 L bench scale laboratory reactor equipped with a steam jacket in continuous steam flow (200 mL/min) conditions. This hydrothermal pre-treatment process organized similar to that which is described in studies of the furfural extraction from birch wood [16, 17]. In these preliminary experiments, temperatures of 160 °C, 170 °C and 180 °C were chosen and the duration of the process was 90 min. Before the process, the raw material was mixed with the calculated amount of the catalyst $Al_2(SO_4)_3$ – 5 wt% of the oven dry sample.

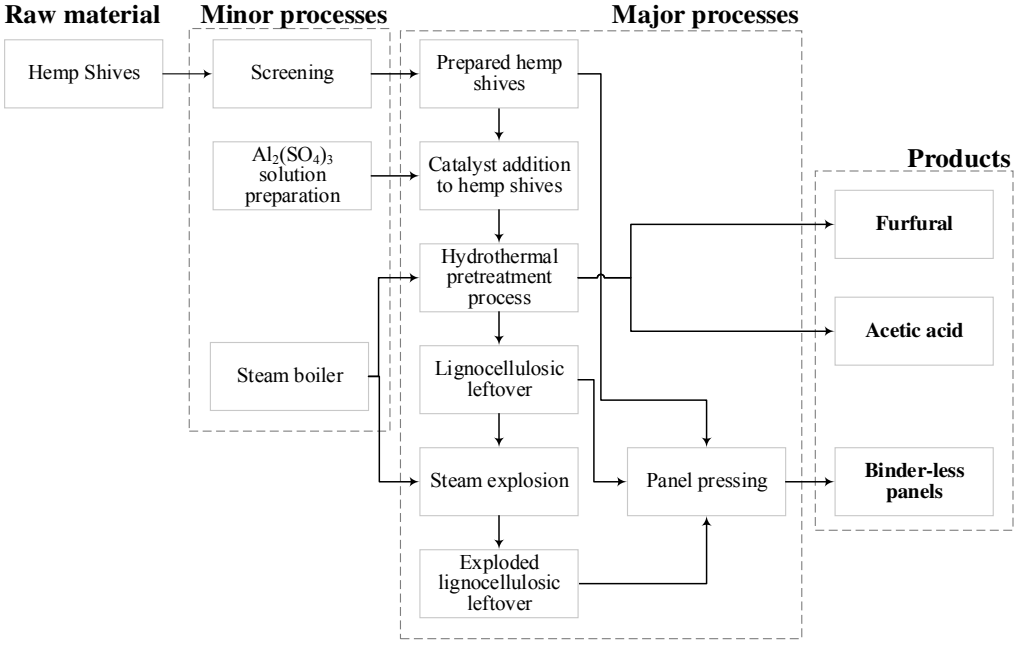

Fig. 1. Complex processing of hemp shives for obtaining of products with a high added value

2.3. Steam explosion

A part of the leftover lignocellulose after the hydrothermal pre-treatment was additionally steam exploded in a 0.5 L batch reactor [11] to liberate the lignin from the cell wall to the fibre surface, since lignin is the most important

component relevant to binder-less panel production [12, 13]. The steam explosion treatment conditions for all pre-treated samples were the same: temperature 235 °C and time 5 s.

2.4. Panel moulding

After pre-treatment and steam explosion treatment, the hemp shives were air dried (25 ± 2 °C) and hot-pressed in a one-stage press under 3 MPa pressure (p), varying the temperature (T), time (t) and moisture content (MC) as shown in Table 2.

Precisely weighed lignocelluloses materials were pre-pressed under 2 ± 1 MPa for 7 ± 3 s using a frame. The pressing conditions were applied for each pre-treated and steam-exploded sample, totally making up 23 panel samples. As the reference material, untreated hemp shives (Ref 1 and Ref 2 in Table 2) were used, pressing under 5 MPa pressure because of the material un-pretreated structure. Four reference panels were made for each pressing temperature. The set density of all samples was 1000 kg/m^3 and the set panel dimensions were 100 × 100 × 7 mm.

Table 2. Panel pressing conditions

Denotation	T, °C	t, min	MC, %	p, MPa
1	150 ± 2	15	10 ± 2	3 ± 0.2
2	160 ± 2	15	10 ± 2	3 ± 0.2
3	160 ± 2	15	5 ± 2	3 ± 0.2
4	170 ± 2	10	5 ± 2	3 ± 0.2
Ref 1	160 ± 2	15	7 ± 2	5 ± 0.2
Ref 2	200 ± 2	15	7 ± 2	5 ± 0.2

3. Results and discussion

After the hydrothermal pre-treatment of hemp shives was mixed with $Al_2(SO_4)_3$, the yield of furfural at 160 °C was 9.4 wt%, but that at 180 °C – 9.7 wt% of the oven dry raw material mass, if the duration of the process was 90 min (Table 3). The yield of furfural did not change significantly with increasing temperature.

Table 3. Results of hemp shives pre-treatment in the presence of $Al_2(SO_4)_3$ depending on the process temperature

Hydrolysis temperature, °C	Hydrolysis condensate			Lignocellulose			
	Furfural, wt% o.d. hemp shives	Acetic acid, wt% o.d. hemp shives	Yield, wt% o.d. hemp shives	Cellulose content, wt% o.d. LC	Cellulose content, wt% o.d. hemp shives	Destruction degree of cellulose, wt%	Holocellulose, wt% o.d. hemp shives
160	9.4	6.4	73.3	42.8	31.4	28.2	34.2
170	9.4	7.1	69.8	38.2	26. 7	39.0	31.4
180	9.7	8.0	65.5	33.9	22.2	49.2	27.7

However, with increasing temperature, the furfural obtaining dynamics significantly increases in the first 10 minutes (Fig. 2 (a)), when the yield of furfural at 180 °C is almost twice as high than at 160 °C. This means that it is possible to decrease the process time by increasing the temperature.

The susceptibility of the lignocellulosic material towards the dehydration of pentoses depends on its ability to generate acetic acid in the reaction media by means of hydronium-catalysed reactions [10]. Therefore, the gradual increase of the process temperature also increased the acetic acid yields (Fig. 2(b)), which means that $Al_2(SO_4)_3$ acts

as a catalyst for deacetylation reactions, which catalyses the xylose dehydration reactions on the surface of hemp shive particles.

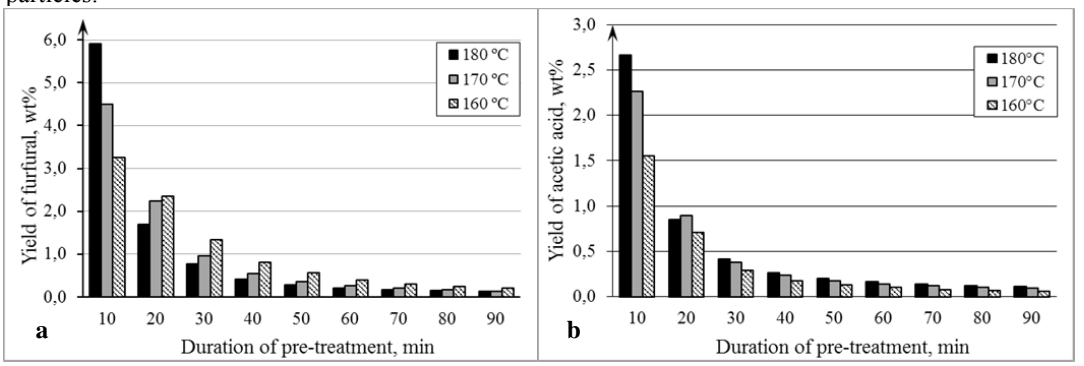

Fig. 2. (a) Dynamics of furfural obtaining and (b) Dynamics of acetic acid obtaining, depending on the pre-treatment temperature

The holocellulose content in the raw material was 75.5 wt% and, after the pre-treatment process, it decreased to 34.2 wt% at 160 °C and 27.7 wt% at 180 °C, calculated on the oven dry hemp shives' mass (Table 2). This means that, during the catalytic pre-treatment in the presence of $Al_2(SO_4)_3$, not only is hemicelluloses converted to furfural, but also some part of cellulose has started to degrade. By increasing the hydrothermal pre-treatment process temperature up to 180 °C, the cellulose content significantly decreased from 31.4 wt% to 22.2 wt%, calculated on the oven dry raw material, taking into account the yield of lignocellulose.

The leftover lignocellulose after the hydrothermal pre-treatment contained ~ 50 wt% moisture content; therefore, it was dried to a 10–15 wt% moisture content at 25°C. With increasing temperature of the pre-treatment process, the moisture content of residual lignocellulose was higher at the drying stage (160 °C – 11.0 %, 170 °C – 17.5 %, 180 °C – 22.8 %). This can be explained by the increasing of the surface of the raw material particles due to the degradation of cellulose at elevated temperatures in the presence of the $Al_2(SO_4)_3$ catalyst (Table 3).

The obtained panels are very different from the outside. The Ref 1 and Ref 2 panels (Fig. 3) are light enough in colour like the raw shives and similar to conventional OSB panels. The panels from the shives after the catalysed hydrothermal pre-treatment process (e.g. HP160_2 in Fig. 3.) are slightly darker in colour, compared to the reference panels. The panels from the pre-treated and steam-exploded shives (e.g. HP160_SET_3 in Fig. 3.) are very dark in colour, with an apparent degraded morphology of shives on the surface. Most of the panels from the pre-treated and steam-exploded shives have gaps on the surface (e.g. HP180_3 in Fig. 3.) and on the inside parallel to the surface. These observations allow concluding that the lignocellulosic material after the steam explosion treatment is significantly degraded. However, the degradation level of lignocelluloses depends on both pre-treatment and treatment, and the treatments conditions should be optimised. Cutting edges are another property of the panel quality that was observed, although only qualitatively. The panels made of untreated shives at 160 °C have unstable edges, which drop off. However, the cut edges of the panels made at 200 °C are stable enough. The panels made of pre-treated shives have cut edges similar to those of the untreated ones, although look more stable. Generally, the cut edges of the obtained panels are poor in quality. This is probably due to the too high moisture content of the pressing material and due to the too high steam explosion temperature that results in the too high severity factor of the material and degradation of cellulose. However, we believe that this could be improved by optimising the panel moulding process that is the next goal of the research. Some studies state that it is possible to make a high quality binder-less panel from agricultural species [18–20].

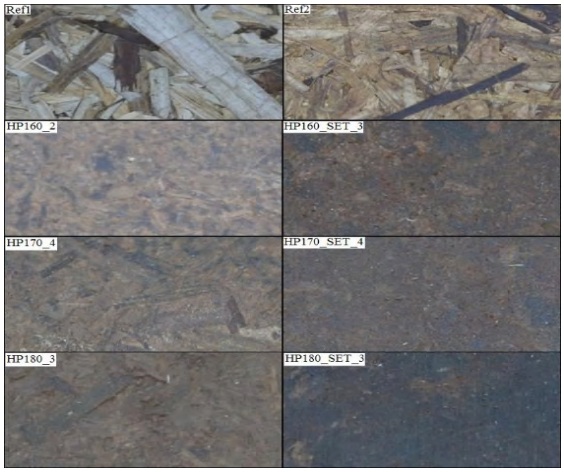

Fig. 3. Binder-less panels made of hemp shives

The density range of all panels obtained was from 800 kg/m^3 to 1250 kg/m^3. 85 % of the differences in density are explained by the panel's thickness, which varies from 6 to 8 mm as shown in Fig. 4(a). On the other hand, such different thickness obtained means that the same pressure used at pressing for all samples shows that the samples are different as materials, and different pressures should be used for each of them to obtain the same density.

The MOR values of the panels vary from 2 (sample HP160_2 in Fig. 3.) to 12 N mm^{-2} (samples Ref 2 and HP180_3 in Fig. 3.), depending on all included factors. However, the strength difference is not significant. The low MOR values could be explained by the high enough severity factor of the lignocelluloses and, possibly, the fact that the pressing temperature was too low to achieve the lignin flowing and then the glass transition necessary to form a rigid material. The MOE values of the panels vary from 141 (sample HP160_2 in Fig. 3.) to 3250 N mm^{-2} (sample HP170_SET_4 in Fig. 3.), also depending on the same factors as in the MOR performance. The obtained maximal MOE value is high enough and demonstrates that the material can be used for panel production. However, the MOR values are too low and should be improved by optimising the panel moulding conditions. In spite of the low mechanical properties, an excellent correlation was obtained between the MOE and MOR values (Fig. 4(b)), which means that the strength of the composites could be predictable.

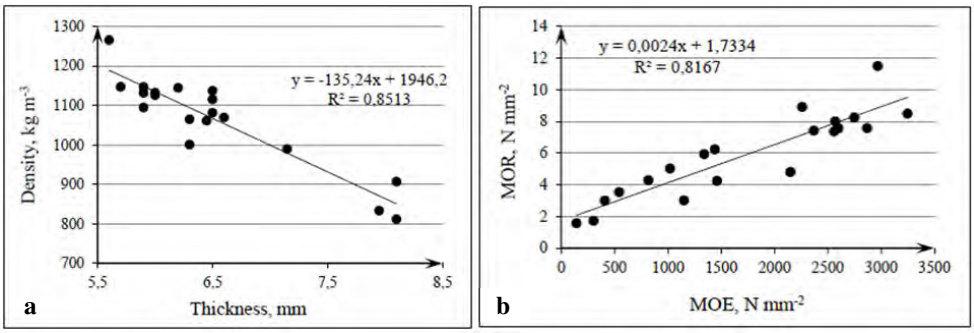

Fig. 4. (a) Panels density vs. thickness; (b) Panels MOR vs. MOE

4. Conclusions

Using $Al_2(SO_4)_3$ as a hydrothermal pre-treatment (160–180 °C) catalyst, it is possible to obtain the yield of furfural 9.4–9.7 wt% from the oven dry raw material mass, and it does not significantly depend on the temperature range if the duration of the process is 90 min. Nonetheless, it is possible to decrease the process time by increasing the temperature. During the catalytic pre-treatment, not only hemicelluloses are converted to furfural but also some part of cellulose has started to degrade.

The gradual increase with the process temperature also showed an increase in the acetic acid yields, testifying that $Al_2(SO_4)_3$ acts as a catalyst for deacetylation reactions, which catalyses the xylose dehydration reactions on the surface of the hemp shives' particles.

It is possible to obtain a binder-less panel from untreated hemp shives as well as from pre-treated ones. However, the panel's manufacturing technology should be improved to obtain composites with better quality and higher mechanical properties. First of all, there should be the diminished moisture content and severity factor of lignocelluloses before the pressing stage. The obtained maximal MOE value (3250 N mm^{-2}) and good enough surface of some panels show that all prepared hemp shives materials can be used for binder-less panel production. The obtained excellent correlation between MOE and MOR values ($r = 0.9$) demonstrates that the strength of the composites could be predictable.

Conflict of interests

A part of the study results was presented at the 22nd International Conference on Composites/Nano Engineering (ICCE-22) on July 15, 2014. The authors have no conflicts of interests due to the contribution of the study and the manuscript text.

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